Chapter 12
Hydrothermal Carbonization of Lignocellulosic Biomass

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Abstract Hydrothermal carbonization (HTC) of lignocellulosic biomass is a pretreatment process to homogenize and densify diverse biomass feedstocks. The solid product is hydrophobic and friable with ultimate analysis similar to that of lignite, and is easily made into durable, dense pellets. Byproducts include aqueous sugars, acids, carbon dioxide, and water. The process consists of treatment in hot (180–280 °C) compressed water for short contact times, and has been demonstrated on woody biomass, agricultural residues, and grasses. HTC reactions include hydrolysis, dehydration, decarboxylation, condensation, polymerization, and aromatization. Nearly all hemicellulose is removed and converted to simple sugars and furfural. Cellulose begins to react at 200 °C, and produces oligosaccharides, glucose, 5-HMF, and organic acids. Lignin is relatively inert. HTC reactions are relatively fast, with reaction times measured in minutes. Both hemicellulose and cellulose degrade by apparent first-order reaction kinetics, where hemicellulose exhibits an activation energy of 30 kJ mol^{-1}, and that of cellulose is 73 kJ mol^{-1}. There has been a flurry of research on HTC published recently, but little commercial activity. Innovative design is required for commercialization, and costs may be high, due to high pressure operation. However, as demand for biomass increases, HTC will surely play a role in enhancing supply chain logistics.

12.1 Introduction

Progressing toward sustainable, renewable energy production is essential for our world in the next century. Fossil fuels, with their irreversible generation of greenhouse gases, cannot provide us with energy indefinitely. Biomass, which

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takes in CO_2 as it grows and uses sunlight as its power source, can play a pivotal role in weaning us from fossil fuels.

Biomass encompasses many types of plant materials. To avoid the food-versus-fuel conflict, only nonfood lignocellulosic biomass is considered appropriate for sustainable energy production. Such biomass includes woody biomass, grassy biomass, and agricultural residues from food production. Lignocellulosic biomass is a many-layered package including lignin, cellulose, hemicellulose, extractives, and inorganics (ash). Converting lignocellulosic biomass to useful forms of fuel presents challenges in handling, storage, and processing. As harvested (often on a seasonal basis), hydrophilic biomass has a high moisture content often rendering it perishable, as well as heavy and thus expensive to transport. Drying can improve storage properties, but is energy intensive. A process to make biomass more hydrophobic would be advantageous. In addition to having high moisture content, biomass is low in energy density compared to fossil fuels. Lignocellulosic biomass has a higher heating value (HHV) of 14–21 MJ/kg, while coal's HHV ranges from 23–28 MJ/kg, and crude oil has an HHV of roughly 45 MJ/kg [1, 2]. Increasing the energy density of biomass would make its use more practical, and would facilitate supply chain logistics. Liberating the cellulose monomer glucose from the lignocellulosic bundle would allow its use in fermentation to ethanol, presently widely added to gasoline.

Applying HTC to biomass overcomes the challenges posed by biomass conversion. HTC makes biomass hydrophobic, enhancing its drying and storage properties, increases its energy density, and releases glucose and other sugar monomers into an aqueous phase, permitting their subsequent upgrading to chemicals and fuels [3–8]. Immersing biomass in liquid water, a treatment especially amenable to moist biomass feedstocks, at temperatures of 180–280 °C, at pressures of 1–5 MPa for as little as 5 min can dramatically improve the fuel properties of the biomass, as well as convert hemicellulose and cellulose to available sugar monomers. The HTC process has the potential to give biomass a significant role in reducing the use of fossil fuels.

12.2 Background

HTC is also known as hydrothermal carbonification, coalification, hydrothermal coalification, hydrothermal treatment, hot-compressed-water hydrolysis, liquid hot water pretreatment, aqueous pyrolysis, aqueous phase carbonization, hydrothermolysis, and wet torrefaction. Its solid product can be called hydrochar, char, HTC char, biochar, bio-coal, or biocarbon. This multiplicity of names for the same process and its solid product can make finding useful data in the literature challenging. HTC produces a liquid byproduct which contains sugar monomers and their decomposition products, and organic acids, as well as CO_2 gas.

Friedrich Bergius [9, 10] first investigated what he called hydrothermal carbonification of biomass or its components in 1913. By heating cellulose in water under pressure, his team obtained a black, coal-like substance. Further research and dispute about whether cellulose or lignin contributed more to "coalification" continued until the 1980s, with the van Krevelen diagram for biomass and coal being the most useful concept produced [11–17]. Dirk Willem van Krevelen evaluated biomass and coal by plotting hydrogen:carbon atomic ratios as a function of the oxygen:carbon atomic ratios, with points closer to the graph origin representing higher fuel value. Thus, the effectiveness of HTC could be determined in terms of fuel enhancement [18–20]. Niesner et al. [21] also pioneered an effective method using HPLC to identify the hydrothermal degradation products of hemicellulose and cellulose from wheat straw.

In the 1980s, the National Renewable Energy Laboratory (NREL) sponsored a Lawrence Berkeley Laboratory project that used conditions similar to HTC, but since liquefaction was the object of the study, the project was discontinued [22, 23]. In 1982, Fuel published Herman Ruyter's work, which emphasized "coalification's" removal of CO_2 and H_2O to improve fuel value and increase hydrophobicity. Ruyter reported results for various biomass from autoclave work, where temperature was varied from 175 to 350 °C, with pressure being the vapor pressure of water at these temperatures. He called attention to the complexity of the mechanisms involved, but nevertheless attempted to quantify the "enrichability" of a biomass as a function of O/C ratio, HHV, and mass yield, the ratio of biochar produced to raw feedstock [24]. In 1983, Bonn et al. [25] described their use of a 2-stage hydrothermolytic process used on poplar wood and wheat straw. The first stage at 180 °C removed the easily hydrolysable polysaccharides (likely hemicelluloses), while the second stage at 260 °C hydrolyzed cellulose to glucose. The overall reaction time was less than 1 h. Schwalde et al. [26] reported their use of HPLC and gel permeation chromatography in determining more accurately the carbohydrates produced from HTC of cotton waste materials. To simplify the complicated reaction scheme of HTC, researchers in the late 1980s and early 1990s performed high temperature/high pressure studies on pure components of biomass, such as cellulose or lignin [27–29]. However, the matrix nature of lignocellulosic biomass prevented easy answers to the complexities of HTC.

In recent years, HTC has become a process more widely recognized to enhance biomass' energy density, friability for homogenized handling characteristics of varying biomass, and hydrophobity for improved storage and transportation properties. In addition, sugar monomer production (at HTC temperatures less than 230 °C) provides a valuable byproduct for possible conversion to liquid biofuels. Practices of HTC vary, but all such processes use subcritical water at temperatures above 150 °C, below which reaction does not substantially proceed. HTC temperatures of 180–280 °C appear to be most practical. Pressures above the water vapor pressure at a given reaction temperature must be maintained, so that the water remains in its liquid state. The biomass feedstock must be submerged in the liquid water, rather than floating above it, with subcritical liquid water serving as solvent, reactant, and catalyst. Reaction times vary from as short as 1 min to as long as 72 h. Water to biomass (w/w) ratios of 5:1–20:1 may be used. Batch processing and continuous processing have been used, with the latter considered economically feasible at large scale. Two-stage processes, which use a lower temperature to obtain sugar monomers, and then a higher one to encourage biochar formation have been proposed. For the HTC solid product, biochar, the main process outputs of concern are mass yield, the ratio of biochar produced to raw feedstock, and energy densification, the ratio of the HHV of the biochar to the HHV of the raw feedstock. Optimization of process conditions for HTC, particularly for specific biomass, remains an active area of research. The knowledge thus gained will be a helpful guide to commercialization for this valuable step in the renewable biomass to energy conversion process.

12.3 HTC of Biomass Components

12.3.1 Cellulose

Cellulose is the most abundant renewable organic material on earth, with an annual production of over 50 billion tons [30]. Plants typically consist of 30–50 % cellulose on a dry basis. Cellulose is a straight chain polysaccharide consisting of glucose residues linked with $\beta-1\rightarrow4$ glycosidic bonds, with hundreds to thousands of glucose repeating units. These glycosidic bonds can be broken by protonation of the oxygen between glucose units or the cyclic oxygen [31]. Hydroxyl groups on the glucose units hydrogen bond with oxygen units on the same or adjacent polymer chains, so that a group of chains form microfibrils of high rigidity and crystallinity. However, microfibrils are formed by microcrystals connected and surrounded by amorphous cellulose chains of varying lengths [30, 32, 33]. Amorphous portions of cellulose polymers often are in random coil conformations [34].

The amorphous parts of cellulose can be hydrolyzed to oligomers of 4–13 degrees of polymerization (DP) using HTC at temperatures as low as 100 °C, but temperatures higher than 150 °C are necessary to break amorphous cellulose oligomers to their monomer components. Crystalline cellulose portions are much less reactive under HTC conditions, due to their strong intra- and intermolecular hydrogen bonds, so that temperatures above 180 °C are required to begin decomposition to glucose monomer [30]. With increased reaction temperature and short reaction time, DP of oligomer varies from 1 (monomer) to a maximal of 23 at 230 °C, 25 at 250 °C, and 28 at 270 °C, suggesting that the glycosidic bonds are attacked randomly on cellulose surfaces [35]. At temperatures above 300 °C, glucose monomer completely decomposes within 5 s, so HTC is impractical if glucose production is desired [36].

At temperatures above 200 °C and times over 5 min, cellulose oligomers progress to glucose monomers that undergo isomerization to fructose, which produces 5-hydroxymethyl-2-furfural (5-HMF), which can be converted to jet fuel, and other products [37]. The main products of cellulose hydrolysis with HTC are glucose, fructose, erythrose, dihydroxyacetone, glyceraldehyde, pyruvaldehyde, and glucose oligomers. Longer reaction times permit increased decomposition products of glucose to form [38]. Cellulose oligomers can also crosslink to form a solid product, particularly at HTC temperatures of 270 °C, and above [35]. For HTC with a reaction time of 240 min at temperature below 200 °C, cellulose can form aggregates of microspheres of about 2.0 μm in diameter [39, 40].

Cellulose particle size and DP can be decreased with ball milling, causing a substantial increase in reactivity with HTC. Hydrogen bond disruption in the crystalline structure may be responsible for this phenomena [41].

12.3.2 Hemicelluloses

Hemicelluloses are the second most common natural polysaccharides, after cellulose, making up 10–35 % of biomass [42]. The polymer chains of hemicelluloses have short branches, are amorphous, and consist of several possible monosaccharide units, including pentoses (xylose and arabinose) and hexoses (glucose, mannose, and galactose). It is commonly acetylated and has side chains of uronic acid and the 4-O-methyl ester [43, 44]. Its low crystallinity due to its branched nature permits it to be soluble in water and generally more reactive than cellulose. Hemicellulose heterocyclic ether bonds are vulnerable to hydrolysis reactions catalyzed by hydronium ions, which are produced under HTC conditions [45]. Hemicelluloses' degree of polymerization varies from 50–200. Xylan is often used as a model hemicellulose compound.

HTC has been performed on beech wood xylan while varying temperature between 180 and 300 °C and reaction time between 0 and 30 min [46]. When the xylan-water mixture was heated to the reaction temperature, a procedure taking ~15 min, and then immediately quenched, xylose and xylose oligomer yield increased from 14 % of xylan reactant at 180 °C to a maximum of 40 % at 220 °C. A second maximum of 42 % occurred at 235 °C, with a rapid decline in yield at higher temperatures. Looking at the effect of reaction time at 220 °C, <5 min reaction time was found to give optimal yield. When HTC was performed on xylan at 235 °C, a very short reaction time (heating to temperature and immediately quenching) gave nearly twice the xylose and xylose oligomer yield compared to a 5 min reaction time [46]. Apparently, temperatures of less than 230 °C and relatively short reaction times are required to hydrolyze hemicellulose using HTC [4, 7, 8, 45]. When HTC was performed on hemicellulose-rich bagasse at 200 °C, only 10 min was needed to maximize xylan to xylose monomer and oligomer yields, with oligomers formed first subsequently decomposing into monomers [38, 46]. Increasing reaction times past 10 min showed reduced xylose yield due to dehydration to 2-furaldehyde (furfural) and other degradation products [38]. Decreasing pH was also found with increasing reaction time for both beech wood xylan and hemicellulose-rich sugarcane bagasse [43, 46]. This phenomena is likely due to liberation of acetyl groups or other organic acid-generating side chains [47, 49]. At lower HTC temperatures (150–160 °C), hemicellulose-rich wheat bran, brewery spent grain, corn cobs, and Eucalyptus wood exhibit xylo-oligomers of structures characteristic of the original biomass, and furfural production is minimal [49].

12.3.3 Lignin

Lignin, the other main component in lignocellulosic biomass, is a three-dimensional, intricately branched structure of high molecular weight (typically > 10,000 Da). It has many hydroxyl and methoxy substituted phenylpropane units. The three most common of these monomers are p-coumaryl, coniferyl, and sinapyl based with ether bonds predominating between these units [38]. Different types of biomass have different ratios of these three monomers, with grasses and softwoods having predominately coniferyl, and hardwoods having a mix of coniferyl and sinapyl. Covalent bonds link lignin with hemicelluloses, enhancing cellulose microfibril protection [50].

Lignin appears to be relatively unreactive under HTC conditions. HTC of lignin (dealkali) at 225, 245, and 265 °C reaction temperatures for 20 h showed lignin to be the least easily decomposed of the main lignocellulosic components, with increasing temperature causing slight decreases in mass yield of solid products [51]. This high yield could be due to lignin's stable phenolic structure. Alternatively, part of the lignin may be decomposed and then undergo self-condensation reactions to reform as insoluble cross-linked polymers [51–54].

When hydrothermal pretreatment is performed on lignin, reaction temperatures higher than typical HTC conditions (180–300 °C) are frequently used. In one such study of alkali lignin, temperatures of 280, 370, 380, and 390 were used with reaction times of 0, 30, 60, 90, 120, and 240 min [55]. At the subcritical reaction temperatures (<374 °C) and the shortest reaction time (immediate quenching,) the main products identified in the liquid phase were guaiacol and vanillin. The solid-phase mass yield was found to be 48.9 % for 280 °C and 25.3 % at 370 °C. Mass yield decreased for these temperatures with increasing reaction time [55]. In another study, a treatment temperature of 304 °C produced 36 % dissolution after 10 min, and 365 °C gave a 90 % dissolution [29].

12.4 Reaction Chemistry

A useful way to depict the effects of both HTC time and temperature is by means of a van Krevelen diagram. This diagram is shown as Fig. 12.1, which plots atomic H/C ratio versus atomic O/C ratio, as commonly used to evaluate the energy quality of solid fuels [20]. Loblolly pine pretreated for 5 min by HTC at 200, 230, and 260 °C are designated as HTC 200, HTC 230, and HTC 260 [56].

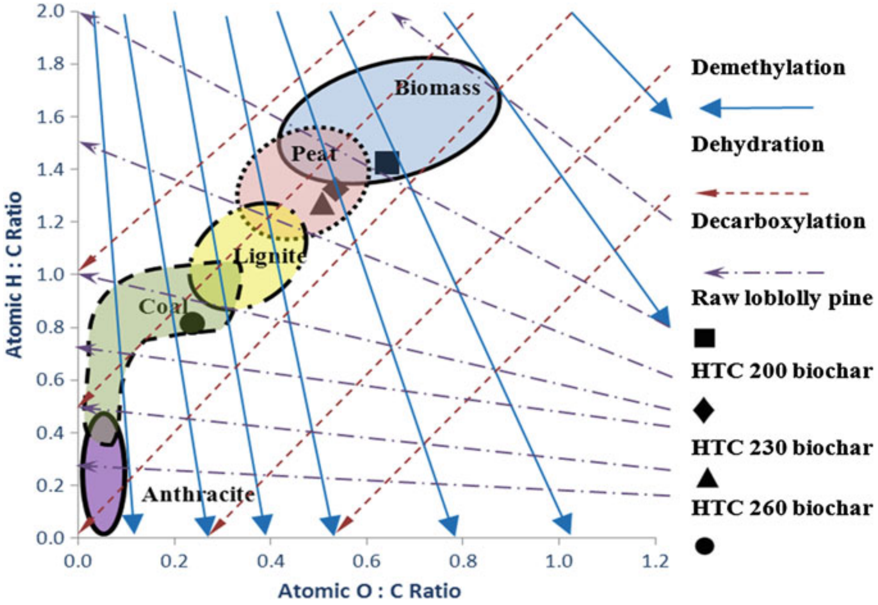


Fig. 12.1 A van-Krevelen diagram of HTC biochars for 5 min reaction time with major reaction lines. Reprinted from [56] with permission

Raw loblolly pine can be found in the biomass region, whereas HTC 200 and HTC 230 are in the peat area and HTC 260 is in the lignite region according to the van Krevelen diagram. It can also be noted that dehydration is the predominant reaction during HTC according to the van Krevelen diagram, although decarboxylation also has some effect. HTC 200, HTC 230, and HTC 260 are in a straight line corresponding to the dehydration reactions [39, 57].

12.4.1 Reaction Mechanisms

12.4.1.1 Hydrolysis

Hydrolytic reactions are the major solid surface reactions, where water reacts with cellulose or hemicellulose and breaks ester and ether bonds (mainly $\beta-(1-4)$ glycosidic bonds), resulting in a wide range of products including soluble oligomers like (oligo-) saccharides from cellulose, and hemicellulose (Fig. 12.2). With increased reaction time, these oligomers further hydrolyze into simple mono- or disaccharides (e.g., glucose, fructose, xylose). On the other hand, 5-HMF and other intermediates might further hydrolyze into simple acids like levulinic, acetic, and/or formic acid [9].

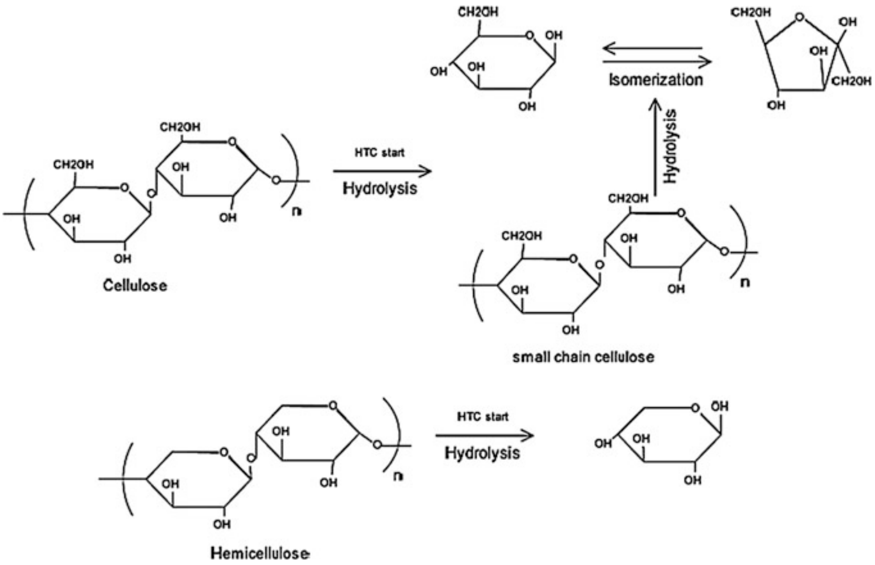


Fig. 12.2 Pathways of cellulose and hemicellulose hydrolysis for HTC. Reprinted from [56] with permission

Hemicellulose starts hydrolyzing at HTC temperatures above 180 °C, but cellulose hydrolysis starts above 230 °C. Liquid water at 200 °C hydrolyzes the β-(1-4) glycosidic bonds of hemicellulose [56, 58], which degrades into sugar monomers, then further degrade into furfurals and other compounds, including 2-furaldehyde [45]. Cellulose can degrade into oligomers, a portion of which hydrolyzes into glucose and fructose due to hydrolysis. Other biomass components like extractives, which are monomeric sugars (mainly glucose and fructose) along with various alditols, aliphatic acids, oligomeric sugars, and phenolic glycosides, are very reactive in hydrothermal media [59]. Lignin and inorganic components are very stable and probably remain unchanged by HTC at 200–260 °C, as discussed above [60].

12.4.1.2 Dehydration and Decarboxylation

Dehydration during HTC can be result from both chemical and physical processes. The physical process is well-known as dewatering, where the residual water is ejected from the biomass during HTC due to the increased hydrophobicity of HTC biochar [3]. Chemical dehydration happens due to elimination of hydroxyl groups [39]. The main reason for this significant decrease in oxygen is the reduction of carboxyl groups, mainly from extractives, hemicellulose, and cellulose. Dehydration and decarboxylation happen simultaneously (Fig. 12.3). One possible path for decarboxylation is the degradation of extractives, hemicellulose, and cellulose.

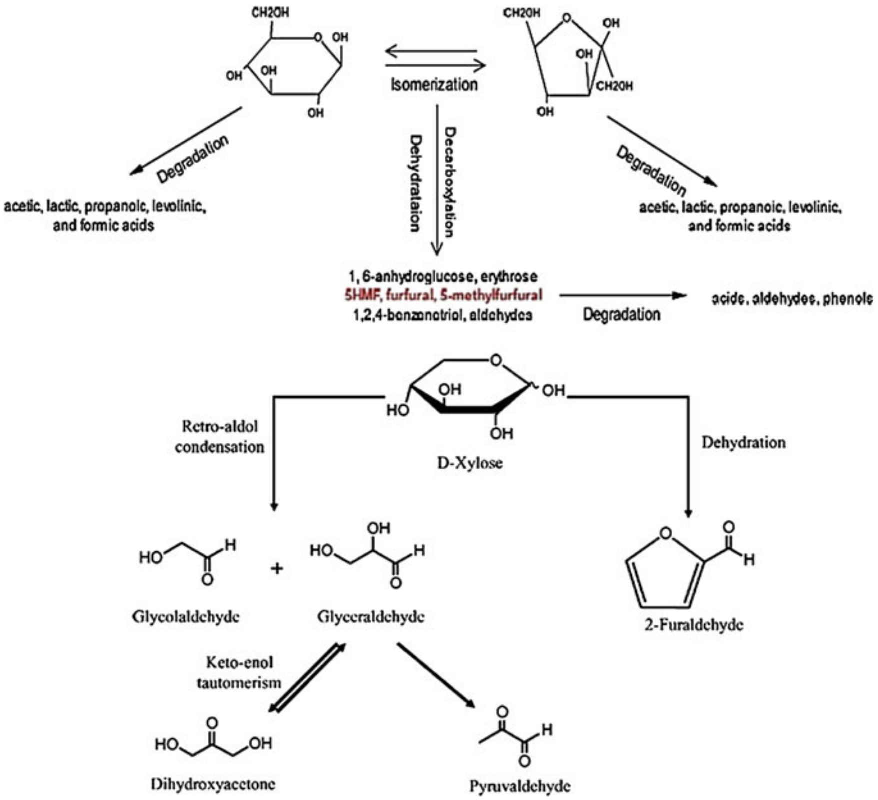


Fig. 12.3 Pathways of degradation, dehydration, and decarboxylation of cellulose, and hemicellulose monomers. Reprinted from [56] with permission

Under hydrothermal conditions, they can degrade into monomers like acetic acid, formic acid, or furfurals, which can further degrade into CO_2 and H_2O [39, 45]. For example, one mole of glucose in an appropriate environment can be converted into 6 moles of CO_2 and 6 moles of H_2O. Thus, the ratio (r) of mol CO_2 to mol H_2O is one for glucose. Similarly, r is defined by other researchers as 0.2–1.0 for cellulose depending on the HTC conditions [9]. Another possible reaction causing dehydration is the degradation of hydrolyzed products from biomass into furfurals like 5-HMF, erythrose, and aldehydes. For instance, each mole of 5-HMF production from glucose yields two moles of water. Moreover, the polymerization of hydrolyzed intermediates can yield water, too. For example, the retro-condensation of 5-HMF into aldol condensation or keto-enol condensation of n monomers yields n moles of water [39]. At the same time, aromatization or polymerization takes place, which also produces significant amounts of water [9].

12.4.1.3 Condensation, Polymerization, and Aromatization

Some of the intermediate compounds (5-HMF, anhydroglucose, furfural, erythrose, 5-methyl furfural) produced from dehydration and decarboxylation reactions of monomers are themselves highly reactive. These intermediates undergo condensation, polymerization, and aromatization as shown in Fig. 12.4. Thus, a linear polymer like cellulose can be converted to a cross-linked polymer similar to lignin. Condensation reactions of monosaccharides are slower, since cross-linked polymerization competes with recondensation to oligosaccharides [9]. Condensation polymerization is most likely governed by step-growth polymerization, which is enhanced by higher temperatures and reaction times [38, 39]. It thus is likely that the formation of HTC-biochar during HTC is mainly characterized by condensation polymerization and aromatization, specifically aldol condensation [38]. Moreover, condensing fragments within the biomass matrix are able to ‘block’ remaining biomacromolecules, thus preventing water access and subsequent hydrolysis, a phenomenon that makes the remaining HTC biochar hydrophobic [45].

12.5 Water Production in the HTC Process

Higher hydrophobicity may contribute to water production with HTC. Lignocellulosic components, being diverse polymers, can be degraded into many components in the HTC process. This results in a reaction mixture with many chemical reactions between different components, making it difficult to model the degradation kinetics. Although literature studies show that hydrolysis, dehydration, decarboxylation, condensation/polymerization, and polymerization reactions occur in parallel in the HTC process, primarily dehydration reactions are found after the initial hydrolysis. To simplify the reaction model and understand the main reactions, Uddin [61] developed an experimental and theoretical approach for the quantification of dehydration reaction of loblolly pine. Figure 12.5 shows that the water production or dehydration increases almost linearly with increasing reaction temperature over the temperature range considered for both 5 and 30 min reaction times. However, the average water production for 5 and 30 min reaction time at 200 °C is negative. Hydrolysis of hemicellulose and cellulose requires one mole of water to produce one mole of dissolved monomeric sugar. On the other hand, two moles of those monomers (e.g. glucose) in the liquid can form one mole of dimer (e.g., sucrose) and one mole of water, or one mole of those monomers can further degrade into lower carbon component and water. If there is no other means of water production in the process then only dehydration or polymerization or degradation to lower carbon component of those dissolved sugars can balance the water used for hydrolyzation. Thus, the possible explanation for a negative water production at 200 °C is that the dehydration reactions are not significant in this case, and further degradation/polymerization of monomers is slow. Cellulose

Fig. 12.4 Pathways of condensation, polymerization, and aromatization of active intermediates. Reprinted from [56] with permission

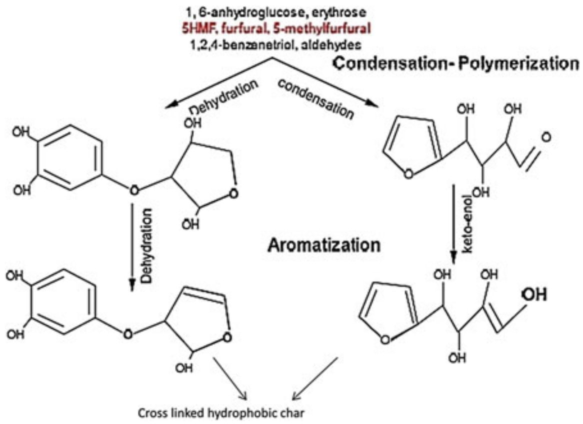
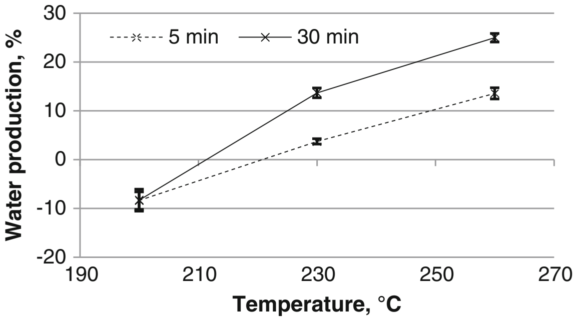

1, 6-anhydroglucose, erythrose
5HMF, furfural, 5-methylfurfural
1,2,4-benzenetriol, aldehydes
Condensation- Polymerization
Dehydration
Condensation
Dehydration
Aromatization
keto-enol
OH
O
Cross linked hydrophobic char

Fig. 12.5 Water production variations of loblolly pine with temperature and time. Reprinted from [61] with permission



decomposition would not start until the temperature is at/over 230 °C. Because the decomposition of hemicellulose starts at a lower temperature (180 °C) than that of cellulose (230 °C) and the degradation of glucose rapidly increases at temperatures >230 °C, the degradation of glucose would be unavoidable if hemicellulose and cellulose are hydrolyzed together [36, 62–64]. For instance, the water production increases from −8 to ~4 % from 200 to 230 °C for 5 min reaction time. This might be the result of simultaneous hydrolysis of hemicellulose and cellulose polymers and decomposition of sugar monomers. A further increase of temperature from 230 to 260 °C increases the dehydration rate, and there is about two times more water production from ~4 to 13.6 % at 260 °C for 5 min residence time.

Based on the solid mass yield, the study also reported that with a long reaction time, the conversion of biomass from low carbon to high carbon content may slow down within 5–10 min, with side reactions occurring in the liquid phase during the remaining reaction time.

12.6 Process Water Recycling

To perform HTC in the most environmentally friendly manner would require recycling of process water, both to reduce the use of fresh water resources and the need for waste-water treatment. Typical HTC practice is to add about four times more water than biomass by weight [6, 19, 63–67]. In an intensive bioenergy production scenario, the supply of process water will be one of the key factors in industrial practice. For example, to produce one metric ton of dry bio-coal from loblolly pine at 260 °C assuming a 60 % mass yield in a batch process would require 8.34 metric tons of water per batch [6]. This large demand for process water can be minimized by recycling it after filtration for a batch or continuous processing system. Another advantage of recycling is that process heat could be recovered, significantly reducing external heating costs. In addition, wastewater treatment costs could be reduced since less wastewater would be generated per kg of feedstock. For both batch and continuous processes, optimization of process water recycling is very important because biomass pretreatment could be affected by the presence of sugars and inorganic materials remaining in the liquid solution. It would be expected that an increase of sugar concentration in the liquid would increase mass transfer resistance for sugar monomers produced from hemicelluloses and cellulose degradation. This hindering of sugar monomer movement to the liquid phase could impede the energy densification aspect of the HTC process.

Stemann et al. [68] first addressed the prospect of water reuse by investigating the recyclability of process water for poplar wood HTC. They found about a 3 % increase of mass yield and 5±1 % increase of HHV for poplar wood at a reaction temperature of 220 °C with a 4 hr reaction time. These researchers expected that the total organic carbon content (TOC) in the liquid phase would increase with recycle number but the results indicated a change in liquid and solid reaction chemistry for later recycles. Stemann et al. [68] described this as an unidentified polymerization of substances.

A similar study was done by Uddin [61] for loblolly pine at three different temperatures (200, 230, and 260 °C) for a reaction time of 5 min. The mass yields data obtained for the three different temperatures with recycling increased about 5 % after the first recycle. The mass yields remained the nearly same for the rest of the liquid recycle experiments compared to the first recycle run. However, HHV values appeared to be approximately constant with increasing recycle numbers for all temperature studied. The water soluble carbonaceous substances are concentrated with successive recycles, but not as much as would be expected to increase the mass transfer resistance, thus increasing the mass yield of the char. The equilibrium moisture content (EMC) results indicated unchanged hydrophobicity of the biochars with recycling process water.

Thus, the recycling of HTC process water appears to be feasible. Recycling will increase mass yield, but not irreparably. If implemented, HTC water recycling would reduce both environmental damage and costs.

Table 12.1 EMC of the HTC biochar pellets at different relative humidities. Reproduced from Ref. [3] by permission of Elsevier

	Treatment temperature (°C)	EMC(%) at $H_R = 11.3$ %		EMC(%) at $H_R = 83.6$ %		EMC(%) at $H_R = 100$ %
		Pellets	Biomass	Pellets	Biomass	Pellets
Raw	–	2.6	3.5 ± 0.5	17.6	15.6 ± 0.9	29.8
HTC	200	1.5	1.8 ± 0.5	12.4	12.8 ± 0.7	27.3
	230	1.0	0.9 ± 0.3	8.6	8.2 ± 0.7	12.6
	260	0.7	0.4 ± 0.3	4.7	5.3 ± 0.03	7.1

12.7 Hydrophobicity

One measure of hydrophobicity is EMC. EMC is defined as the moisture content in the biomass that is in thermodynamic equilibrium with the moisture in the surrounding atmosphere at a given relative humidity, temperature, and pressure. Acharjee et al. [3] performed HTC on loblolly pine at 200, 230, and 260 °C for 5 min. Table 12.1 shows EMC data for these HTC biochar. Their EMC values are lower than those for raw biomass at all relative humidities (HR) tested. This indicates that pretreated biomass, is more hydrophobic than raw biomass. Moreover, it becomes more hydrophobic with increasing process temperature. The explanation offered for this behavior is a combination of removal of aqueous extractives and hemicellulose, which are more hydrophilic than other fractions of biomass, and hydrolysis of -OH groups, thereby leaving behind fewer sites for hydrogen bonding.

12.8 Chemical Characteristics of HTC Biochar from Attenuated Total Reflectance: Fourier Transform Infrared Spectroscopy

HTC biochar has different chemical characteristics than raw biomass. FTIR is an important tool for studying chemical bonds. From Fig. 12.6, raw loblolly pine shows strong bonds at 910, 1050, 1180, 1260, 1390, 1510, 1613, and 1735 cm^{-1} in the fingerprint region. These correspond to aromatic carbon hydrogen bonds of hemicellulose (C–H), alcohol groups of glucose (C–OH), glycosidic bonds of cellulose (C–O–C), aryl-alkyl ethers of lignin ($O\text{-}CH_3$), aromatic acids of hemicelluloses (C–H), ketone groups of hemicelluloses (C=O), aromatic carbon skeletons (C=C), and carboxylic acid groups of hemicellulose (C=O), respectively. A broad aliphatic hydrocarbon or wax (–CH) and aliphatic hydroxyl bond for bound water (–OH) can be observed at 2840–2920, and 3100–3500 cm^{-1} respectively [65]. Both the peaks are found flattened with increasing HTC temperature. In the spectrum of raw loblolly pine, the band at 1725 cm^{-1} due to

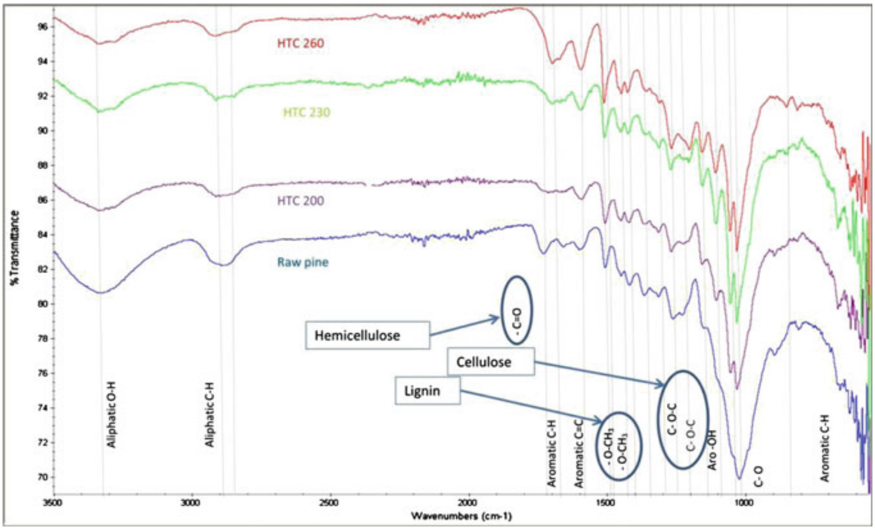


Fig. 12.6 ATR-FTIR spectroscopy of raw loblolly pine and loblolly pine pretreated at 200, 230, and 260 °C. Spectrum closest to the x axis corresponds to raw pine and those farther away are HTC 200, HTC 230, and HTC 260 spectra, respectively. Reprinted from [56] with permission

hemicelluloses [69], cannot be found in the HTC biochar spectrums, possibly due to the degradation of hemicellulose. The band at 1640 cm^{-1} could be assigned to the C=C stretching of aromatic rings or the bending mode of adsorbed water. Only the raw biomass spectrum shows that absorbance, meaning that the raw biomass is more hydrophilic than the pretreated. The peak at 1495 cm^{-1} ($–O–CH_3$) is the characteristic peak for lignin, and the peak is sharpens with increasing HTC temperature, indicating lignin enrichment. The peak at 1374 cm^{-1} weakened with HTC reaction temperature. The spectral peak on the shoulder at 1264 cm^{-1} (C–O stretching of the ether linkage) is the signature of lignin and it sharpens with increasing temperature [57]. Thus, FTIR-ATR of loblolly pine and its biochars from different reaction temperatures give some idea of what kinds of chemical changes occur in biomass with HTC. Such knowledge is useful in modeling the kinetics of the process.

12.9 Kinetics

Chemical reaction kinetics deals with the rates of chemical processes where the potential barrier constitutes the activation energy of the process, and determines the rate at which it will occur at a given temperature. When the barrier is low, the thermal energy of the reactant molecules is high enough to overcome the barrier so that they convert to reaction products rapidly. However, when the barrier is high, only a few reactant molecules will have sufficient energy, so that reaction is slower. Average reactant molecules' thermal energy increases with temperature, so that reaction rate increases with temperature.

HTC of lignocellulosic biomass follows a very complex reaction mechanism, resulting in difficulty in predicting accurate activation energies for the various reactions. For this reason, simplified models of the reactions of cellulose, hemicellulose, and lignin are used when investigating the kinetics of the hydrolysis of lignocellulosic materials.

12.9.1 Kinetic Models of Hemicellulose

The models proposed in the literature use pseudo homogeneous irreversible first-order reactions. Based on the first degradation model proposed by Saeman [70] for cellulose, researchers come up with a two-step first-order reaction model describing hemicellulose hydrolysis kinetics in hydrothermal condition. However, after observing the hydrolysis reaction rate, which decreased significantly after about 70 % conversion, Kobayashi and Sakai [71] introduced a model that included two types of hemicellulose, one fast hydrolyzing and one slow, each with its own kinetic constant. According to this model, the hydrolysis of the hemicellulosic fraction follows the following path [45, 72, 73]:

$$\begin{array}{r}\text{Fast hydrolyse}\overset{\text{yields}}{\rightarrow}\\ \text{Slow hydrolyse}\overset{\text{yields}}{\rightarrow}\end{array}\text{Oligomers}\overset{\text{k1}}{\rightarrow}\text{Monomers}\overset{\text{k2}}{\rightarrow}\text{Monomer products} \tag{12.1}$$

Sarkar et al. [74] measured the degradation of xylose, a hemicellulose monomers, in rice straw in a very dilute acid solution at 100 °C and reported the rate constants (k1 = 0.094 and k2 = 0.006, min^{-1}). A similar study conducted by Rodriguez et al. [75] for wheat straw at 130 °C showed the rate constants (k1 = 0.1068 and k2 = 0.00026, min^{-1}).

12.9.2 Kinetic Models of Cellulose

The dilute acid hydrolysis of cellulose was described by Saeman [71] to understand the kinetics of lignocellulosic materials. The two-step degradation proposed by Saeman was two consecutive first-order reactions:

$$\text{Cellulose polymers}\overset{\text{k1}}{\rightarrow}\text{Glucose monomers}\overset{\text{k2}}{\rightarrow}\text{Monomer degradation products} \tag{12.2}$$

There are two types of hydrogen bonds in cellulose molecules: those that form between the C3 OH group and the oxygen in the pyranose ring within the same molecule and those that form between the C6 OH group of one molecule and the oxygen of the glucosidic bond of another molecule. Ordinarily, the beta-1,4 glycosidic bonds themselves are not too difficult to break. However, because of these hydrogen bonds, cellulose can form very tightly packed crystallites. These crystals are sometimes so tight that water cannot penetrate. This fact was missing in Saeman [70] hydrolysis model of cellulose. Because the amorphous cellulose hydrolyzes almost instantaneously to glucose, an initial glucose concentration must be assumed. This factor is easily incorporated into the original model, and all subsequent models have done so. To incorporate both crystalline and amorphous cellulose, Conner et al. [76] proposed an improved model of glucose degradation in hydrothermal condition. Mok and Antal [77] confirmed that a part of cellulose was nonhydrolyzable under hydrothermal reaction. However, this study concluded that this is due to an acid-catalyzed parasitic pathway that competes with the acid-catalyzed hydrolysis pathway and that there is no significant chemical change in the cellulose itself. Formation of intermediates in hydrothermal pretreatment of cellulose and hemicellulose has been well examined in several studies [76–80].

12.9.3 Kinetic Models for Lignin

Lignin being a large cross-linked polymer can be degraded into tens of components resulting in a large number of chemical reactions between different components in the reaction mixture, which make it difficult to model the degradation kinetics. Bobleter and Concin [78] first proposed two phase degradation kinetics of poplar lignin. The first phase reactions are very rapid, even less than 1 min, where lignin is degraded into soluble fragments, mainly consisting of low molecular components (e.g., monomers) and higher molecular components (oligomers). In the second phase (slower), the condensation reactions between soluble components and/or insoluble polymers produce insoluble polymers and char. In both cases, they assumed first-order degradation and condensation.

$$\text{Lignin} \overset{\text{k1}}{\rightarrow} \text{Monomers} + \text{Oligomers} \overset{\text{k2}}{\rightarrow} \text{Insuloble polymers} + \text{char} \tag{12.3}$$

According to Bobleter and Concin, the insoluble polymer exists during the first phase of quick reaction as a homogeneous suspension, which also reacts with the reactive soluble part.

Based on this model, Zhang et al. [81] proposed similar kinetic model for the hydrothermal degradation of Kraft pine lignin, where they assumed that a part of the soluble fragments reacts with all soluble components in the reaction mixture to form the insoluble polymers and char in the second phase. The estimated activation energy for lignin degradation is 37 kJ/mol for a temperature range of 300–380 °C. However, it should be noted that this model could not be directly used in hydrothermal treatment of the other biomass. Modification of the model is required to ensure the accuracy of model prediction when applied to the other biomass.

12.9.4 Model Proposed by Reza et al. [107] for Loblolly Pine

Under specific HTC conditions the lignin, cellulose, and hemicellulose fractions in lignocellulosic biomass follow distinct paths [82]. For pure components, reaction paths and their corresponding activation energies are available in the literature. However, when packaged in the lignocellulosic biomass matrix, these components may express different activation energies. One reaction can affect the other, resulting in a change of activation energy for the individual components. Reza et al. [60] proposed a simple kinetic model, consisting of two parallel first-order reactions, to calculate the activation energies of cellulose and hemicellulose of loblolly pine assuming the water extractive reactions are instantaneous.

$$\text{Extractives} \rightarrow \text{Soluble} + \text{Gas} \tag{12.4}$$

$$\text{Hemicellulose} \rightarrow \text{Soluble sugars} + \text{Gas} \tag{12.5}$$

$$\text{Cellulose} \rightarrow \beta\,\text{Bc} + (1-\beta)(\text{Soluble sugar} + \text{Gas}) \tag{12.6}$$

where Bc, represents solid products from cellulose decomposition. Cellulose does not decompose completely and the mass yield of biochar from cellulose is denoted by the parameter β in the third reaction. The rates of decomposition of both hemicellulose (H(t)) and cellulose (C(t)) are both described by the first-order reaction kinetics, where k_1 and k_2 are the rate constants for the two reactions.

$$\frac{d\text{H}(t)}{dt} = k_1\text{H}(t) \tag{12.7}$$

$$\frac{d\text{C}(t)}{dt} = -k_2\text{C}(t) \tag{12.8}$$

The solution of these equations is shown below, with the initial component mass at time zero indicated by a zero subscript. The expression for the functions of H(t), C(t), and Bc(t) are function of reaction time but the function of L(t) is expressed as a constant as lignin is considered an inert component.

$$\text{H}(t) = \text{H}_0 e^{-k_1 t} \tag{12.9}$$

$$\text{C}(t) = \text{C}_0 e^{-k_2 t} \tag{12.10}$$

$$B_c(t) = \beta C_0(1 - e^{-k_2 t}) \tag{12.11}$$

$$L(t) = L_0 \tag{12.12}$$

where H_0, C_0, and L_0 represent the initial mass of hemicellulose, cellulose, and lignin in loblolly pine, respectively. If M(t) represents the mass of unreacted biomass plus solid-phase reaction products at time t, M(t) can be written by

$$M(t) = H(t) + C(t) + B_c(t) + L(t) \tag{12.13}$$

To express the mass yield of biomass Y(t), Eq. (12.13) can be rewritten as Eq.12.14

$$Y(t) = \frac{M(t)}{M_0} = Y_{H0}e^{-k_1 t} + Y_{C0}e^{-k_2 t} + \beta Y_{C0}\left(1 - e^{-k_2 t}\right) + Y_{L0} \tag{12.14}$$

To determine the mass yield of biomass by equation (12.14), the value of β is needed at any time t. If t tends to infinity then equation (12.14) will be written as Equation (12.13), without considering aqueous extractives:

$$\lim_{t \to \infty} Y(t) = \beta Y_{C0} + Y_{L0} \tag{12.15}$$

Equation (12.15) is independent of HTC temperature if β is a temperature-independent parameter. To evaluate β and determine its dependency on HTC temperature, HTC reactions for extended periods (10, 15, and 30 min) were performed at 200, 230, and 260 °C and the value calculated was 0.54.

To calculate the rate constants k_1 and k_2, the mass yields of loblolly pine were measured experimentally for various reaction times at a specific HTC temperature.

The best fit for rate constants can be obtained by minimizing the objective function $F(k_1, k_2)$.

$$F(k_1, k_2) \equiv \sum_{i=1}^{n} \left(Y_i^{\text{experimental}} - Y_i^{\text{model}}(k_1, k_2)\right)^2 \tag{12.16}$$

where Yi experimental represents the experimental mass yield and Yi model represents the mass yield as calculated in Eq. 12.14.

An Arrhenius plot (Fig. 12.7) of these rate constants generated the degradation activation energies of hemicellulose and cellulose of loblolly pine in the HTC process. The activation energies were reported to be 29 $\text{kJ}\cdot\text{mol}^{-1}$ for hemicellulose (rate constant k_1), and 77 $\text{kJ}\cdot\text{mol}^{-1}$ for cellulose (rate constant k_2). The higher activation energy for cellulose compared to that of hemicellulose is consistent with data reported elsewhere [45, 82], indicating the greater recalcitrance of cellulose. The numerical values for activation energies are smaller than those for pure hemicellulose and cellulose (129–215 kJ/mol) in this temperature range [82, 83].

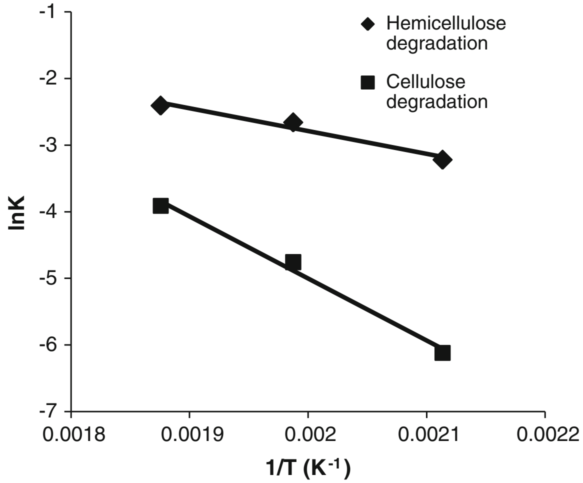


Fig. 12.7 Arrhenius plot for HTC reaction kinetics. Reprinted from Ref. [60], Copyright 2013, with permission from Elsevier

Instantaneous degradation of aqueous extractives likely reduces the pH of the solution and thus enhances degradation of hemicelluloses and cellulose [4], while hemicellulose degradation results in even greater acid production, further catalyzing cellulose reactions. As a result, the individual activation energies for both hemicellulose and cellulose are lower than those for the pure forms not encased in a lignocellulosic biomass package. Lignin, in this simple kinetic model, is assumed inert, but since the activation energies of hemicellulose and cellulose are lower in lignocellulosic biomass than in their pure form, so lignin activation energy in biomass may also be reduced. Torrefaction is another practice for thermally carbonizing lignocellulosic biomass. Prins et al. [84] reported a kinetic study of torrefaction of lignocellulosic biomass assuming similar first-order reactions for hemicelluloses and cellulose, and reported activation energies of 76 and 152 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Compared to the (dry) torrefaction results (Yan et al. [85]), HTC kinetics in this study are more rapid, likely due to the reactivity of high temperature water.

12.10 HTC of Lignocellulosic Biomass Types

Lignocellulosic biomass comprises many different types. Different biomass have varying proportions of cellulose, hemicelluloses, and lignin, with the latter two categories containing various chemical components and side groups. HTC process variables may need to be optimized to obtain a desired result for a given lignocellulosic biomass. This section describes literature data on HTC of “woody” biomass, “grassy” biomass, and biomass obtained from agricultural residues.

12.10.1 HTC of Woody Biomass

"Woody" biomass is composed of 38–55 % cellulose, 15–30 % hemicelluloses, 15–30 % lignin, 2–5 % extractives, and less than 5 % inorganics (ash) [86]. Acetylated galactoglucomannans are the main softwood hemicelluloses [87], while hardwood hemicelluloses are predominately xylans [88]. Lignin type differentiates hardwoods from softwoods, with softwoods possessing guaiacyl phenylpropanoid almost entirely, and hardwoods a mixture of syringyl and guaiacyl phenylpropanoids. Hardwoods also have large pores, or vessels, absent in softwoods.

12.10.1.1 HTC of Hardwoods

Softwoods are generally less expensive than hardwoods, which are valued for construction as well as fuel. Nevertheless, HTC has been investigated for the hardwoods chinquapin, aspen and forest mangrove. With a flow-through reactor with temperature increased by stages to 285 °C, Ando et al. [89] found for the hardwood chinquapin that hemicellulose was solubilized by 180 °C, and cellulose by 230 °C, with a reduction in solvent pH to 4. The end pH value for the aqueous phase indicates production of organic acids from the biomass, reflecting the type of hemicellulose it contains. The 30 % lignin in the raw biomass was mostly solubilized, as well. These authors claimed that hardwood lignin was easier to decompose than softwood lignin. For aspen (Populus tremuloides) and a flow-through reactor with two temperature stages, Bonn et al. [25] reported that hemicellulose was hydrolyzed at 180 °C after 30 min, but cellulose required a reaction temperature of 265 °C for 30 additional minutes. A final mass yield of only 5 % was obtained, indicating that most lignin must have been degraded. For a 300 °C for 30 min batch hydrothermal pretreatment of forest mangrove (acacia magium), Nonaka et al. [90] found the solid product to be more hydrophobic, a 91 % mass yield, but an energy densification of 140 %. Thus, polymerization of solubilized components is likely to occur at this high HTC temperature to achieve such an enhanced energy densification with a high mass yield.

12.10.1.2 HTC of Softwoods

The effects of HTC have been investigated on softwoods, including Japanese cedar (Cryptomeria Japonica). Phaiboonsilpa et al. [91] used a two-step semi-flow hot-compressed water first at 230 °C for 15 min and then at 280 °C for 30 min on Japanese cedar. At 230 °C, nearly all the hemicelluloses were hydrolyzed, as well as about half the lignin, with cellulose only 10 % hydrolyzed. The 280 °C for 30 min step removed the remaining cellulose from the solid residue, leaving only 12 % as a lignin residue. In a flow reactor, HTC was performed by Ando et al. [89] on Japanese cedar at 180 °C for 20 min, then 285 °C for 7 min. Again, hemicelluloses were hydrolyzed at 180 °C and about half of the lignin, with a lignin residue of 12 % remaining, nearly twice as much as for the same process done with hardwood. The pH value for this softwood was about 4.5, slightly higher than for the hardwood chinquapin described in the previous paragraph. Nonaka et al. [90] investigated hydrothermal pretreatment of Japanese cedar using both flow and batch methods at 300 °C for a 30 min reaction time. Both reactor types gave the same mass yield of 89 %, and similar energy densifications of 140 %, as well as increased hydrophobicity. Thus, scaling up to a more economical continuous HTC process may be quite feasible. Overall, Japanese cedar softwood gives results similar to hardwood, except that its lignin is more resistant to hydrolysis.

Using a batch reactor at 200, 230, or 260 °C for 5 min, Yan et al. [8] performed HTC on loblolly pine, a softwood of less than 1 % ash from the southeastern United States. They reported that EMC, a measure of hydrophobicity, decreased with increasing HTC reaction temperature. EMC was reduced to less than a third of the raw loblolly pine's value. Mass yield also decreased, from 90 to 57 %, with increasing reaction temperature. Energy densification increased from 110 to 140 % with increased reaction temperature. As with hardwood and Japanese cedar, all hemicellulose is solubilized by HTC even at the lowest temperature of 200 °C. Cellulose is hydrolyzed more (from 22 to 64 %) with increasing HTC reaction temperature. For loblolly pine, lignin does not decompose at 200 °C, and only undergoes 15 % conversion at 230 °C and 23 % at 260 °C. However, Yu and Wu [30] have suggested that repolymerization of cellulose, producing a pseudo-lignin compound detected by fiber analysis, may account for the apparent inert behavior of lignin in HTC. Loblolly pine has an unusually high amount of cellulose (55 %), so if solubilized fragments polymerize into a pseudo-lignin, the effect could mask lignin decomposition.

Lynam et al. [92] reported similar results for mass yield and energy densification for HTC of loblolly pine for the same reaction conditions, as well as remarking on the friability of the solid product. Scanning electron microscope (SEM) images of loblolly pine raw and pretreated at 200, 230, and 260 °C indicate the stripping of hemicellulose from the lignocellulosic matrix at 200 °C, and the stripping of cellulose at 260 °C. In addition, Lynam et al. (2013) determined that reaction temperature was the most significant variable for HTC, compared to reaction time, water to biomass ratio, and loblolly pine particle size. The work of Lynam et al. [4] on loblolly pine suggested that increasing temperature caused more dehydration of glucose to 5-HMF, a product of greater HHV, which would deposit in the pores of the now friable, higher surface area biochar to increase its HHV. This work indicated that loblolly pine HTC at 230 °C for 5 min reduced pH to 3 in the solvent.

Kang et al. [51] investigated pine wood meal HTC at 225, 245, and 265 °C using a reaction time of 20 h. Mass yield for all three reaction temperatures was ~55 %, but energy densification increased from 148 to 162 % with increased temperature. Since Reza et al. [60] suggest that reactions in the solid product are complete within 5 min and that mass yield for loblolly pine reaches a minimum of 55 %, 20 h may not be an economical option for a reaction time.

Using a mix of Jeffrey Pine and White Fir (called Tahoe Mix) obtained from the Tahoe Forest in California, USA, Hoekman et al. [19] investigated reaction temperatures of 215, 235, 255, 275, and 295 °C for 30 min reaction times, as well as 5, 10, 30, and 60 min reaction times at a reaction temperature of 255 °C, using a batch reactor with stirring. Increasing temperature decreased mass yield from 69 to 50 %, while increasing time for a 255 °C HTC temperature only decreased mass yield from 58 to 52 %. Again, the significance of reaction temperature compared to time is illustrated. With increasing temperature for a 30 min reaction time, energy densification increased from 111 to 145 %. With increasing reaction time at 255 °C, energy densification increased from 123 to 143 %. The end pH for all reaction conditions was about 3. Lynam et al. [92] also investigated Tahoe Mix, using 200, 230, and 260 °C and a 5 min reaction time in an unstirred batch reactor. Mass yield at similar temperatures, although showing a decrease with increasing temperatures, was ~15 % higher. This discrepancy in mass yield is likely due to the shorter reaction time or to the lack of stirring in the reactor.

Overall, softwoods give results for HTC similar to hardwoods, except that softwood lignin is more resistant to hydrolysis. HTC hydrolyzes the hemicellulose of both types of woody biomass at temperatures near 180 °C and cellulose at higher temperatures. To remove substantial amounts of lignin requires even higher temperatures. The solvent end pH value decreases to 3–4 due to organic acid formation.

12.10.2 HTC of Biomass from Grasses

Although grasses may vary in cellulose, hemicellulose, and lignin proportions, nearly all of them have more ash content than woody biomass, which can cause difficulties when used as an energy resource. In recent years, interest in switchgrass, which is ~7 % ash, as an energy crop has intensified. Pretreating it using HTC was studied by Lynam et al. [92] at 200, 230, and 260 °C with a 5 min reaction time. Likely due to the percentage of hemicellulose (31 %) being much higher than that of a typical biomass, HTC of switchgrass gave a mass yield at 230 and 260 °C much lower than that of the softwoods loblolly pine and Tahoe mix. For a 260 °C reaction temperature, a mass yield of only 30 % was achieved. However, for reaction temperatures of 230 and 260 °C, energy densifications were reported to be 112 and 133 %, respectively.

HTC of miscanthus, also known as elephant grass, was investigated by Chiaramonti et al. [93] at temperatures in the range of 150–230 °C. These authors describe HTC reaction conditions in terms of “severity”, a mathematical combination of reaction time and temperature used. Since no significant interactions between time and temperature with HTC have been reported, such a severity approach has its difficulties [92]. Miscanthus also has high hemicellulose (27 %) and an ash of 3 %. With HTC, mass yields of 70–90 % were obtained with a rapid reduction in hemicellulose with increasing HTC temperature and time, while cellulose and lignin remained intact. To summarize, grassy biomass, despite having higher ash than woody biomass, appears to react in similar ways, except that lower mass yield was found with HTC, particularly for switchgrass.

12.10.3 HTC of Agricultural Residues

Agricultural residues vary widely in type and composition, from straws, corn stover, and sugar cane bagasse to rice hulls, sunflower stems, and coconut fiber. HTC can make solid fuel out of these byproducts that are required to grow food, so that land resources can be used to produce both food and fuel simultaneously.

HTC of wheat straw, of 6.5 % ash, has been investigated by Petersen et al. [58] using a 50 kg/hour continuous flow system at temperatures of 185, 195, and 205 °C for 6 or 12 min. As might be expected for HTC temperatures near 200 °C, cellulose and lignin remain in the solid product, while hemicellulose is hydrolyzed. The amount of hemicellulose remaining in the solid product varies from 70 to 30 % as temperature and time is increased from185 to 205 °C and from 6 to 12 min. This sensitivity of hemicellulose conversion to slight changes in temperature and time points to their importance in HTC processes for straw-type biomass. Using rye straw (6 % ash), Rogalinski et al. performed HTC using both a batch reactor and a continuous reactor [94, 95]. In the batch reactor HTC at 190 °C for 120 min gave a mass yield of 75 %. With the continuous reactor, temperature ranged between 120 and 310 °C and residence time between 1.0 and 14.5 min, while pressure was held at 100 bar. Increasing temperature and time decreased mass yield from 95 to 50 %. These authors reported that rye straw particle size and water to biomass ratio seemed to have no influence on mass yield.

Lynam et al. [92] investigated the effects of HTC on the agricultural residues of corn stover and rice hulls) at 200, 230, and 260 °C with a 5 min reaction time. For both biomass, mass yield at 200 and 230 °C was reported to be about 90 and 75 %, respectively. Energy densification for the two were near 100, 105, and 125 % at 200, 230, and 260 °C, respectively. These similarities may relate to the high ash content of corn stover, 7 %, and rice hulls, 21 %. However, at 260 °C, the 43 % mass yield of corn stover was much lower than for rice hulls or the woody biomass loblolly pine and Tahoe mix. At this higher HTC reaction temperature, corn stover behaved much more similarly to switchgrass. A primary agricultural residue, corn stalks and leaves would seem less closely related to the secondary agricultural residue rice hulls, the siliceous husks of rice grains and more closely related to grassy biomass. Mosier et al. [96] investigated corn stover using a continuous HTC process at reaction temperatures of 170, 180, 190, and 200 °C. Slight decreases in mass yield were seen with reaction time increase from 5 to 20 min, but mass yield decreased from 90 % at 170 °C to 60 % at 200 °C. This kind of sensitivity of mass yield to temperature may be a characteristic of grassy agricultural residues.

Sugarcane bagasse has been widely studied as an energy resource. Chen et al. [97] performed HTC on bagasse at 180 °C for 5, 15 and 30 min using a batch reactor. Increasing reaction time decreased mass yield from 70 to 61 %, but had no effect on energy densification, which was 110 %. Hemicellulose was solubilized at this temperature. Increasing temperature from 200 to 280 °C and using a semi-batch reactor, Sasaki et al. [98] demonstrated that extractives and hemicelluloses were extracted from bagasse between 200 and 230 °C, while cellulose was solubilized between 230 and 280 °C.

HTC of more exotic agricultural residues have been investigated. Lui et al. [99] performed HTC at 150–350 °C in a batch reactor for 30 min on coconut fiber (~5 % ash) and dead eucalyptus leaves (~7 % ash) due to their high production potential in Singapore. With increasing reaction temperature, mass yield declined for both biomass from 90 % at 150 °C to 30 % at 350 °C, with little effect on mass yield seen above 300 °C. Energy densification increased from 134 % at 220 °C to 160 % at 300 °C, but declined with further temperature increase for both biomass. The researchers claimed higher hydrophobicity with increasing HTC reaction temperature. Roman et al. [100] studied the effects of HTC on sunflower stems and walnut shells at190 and 230 °C for reaction times of 20 or 45 h. Results showed that increasing time from 20 to 45 h had no effect, as one might expect for HTC. For sunflower stems, increasing temperature decreased mass yield from 40 to 29 % and increased energy densification from 149 to 176 %, exhibiting a remarkable increase in HHV. For walnut shells (~6 % ash), increasing temperature decreased mass yield from 50 to 35 %, while energy densification from 118 to 150 %. Considering the low temperatures, HTC seems quite effective in enhancing the solid products of these less studied biomass.

In summary, the diversity of agricultural residues makes them hard to generalize. However, agricultural residues perform more similarly to grassy biomass than woody biomass when undergoing HTC. Their sensitivity to small reaction temperature changes is noteworthy. Mass yields for these biomass tend to be lower, particularly at higher reaction temperatures. Agricultural biomass are also similar to grassy biomass in that both have higher ash (inorganic) content than woody biomass.

12.11 Inorganic Analysis of Lignocellulosic Biomass and Its Biochars

Plants acquire inorganics, which are necessary for their metabolic pathways, from the soil in which they are grown. Inorganics are in the form of inorganic salts, bound to the organic structure by ionic bonds, or possibly covalent bonds, in a cross-linked matrix [101]. Woody biomass contains less inorganic content than grasses or agricultural residues [102, 103]. Due to their high melting points, the inorganics usually remain in the ash, which may have a negative impact on biomass firing or even co-firing with coal [104]. During combustion, ash must be removed from the boiler, as it increases the complexity in co-firing as well as lowers the efficiency of the boiler. Moreover, sodium, potassium, calcium, and other metals can cause slagging and fouling, resulting in lower power plant efficiency [101, 105]. Chloride, which is very corrosive for stainless steel, can also react with alkalis and silicates to form an undesirable stable slag [103]. Heavy metals like mercury, lead, arsenic, chromium, copper, zinc, and selenium are scarce in biomass. Slagging is the formation of molten or partially fused deposits on furnace walls or convection surfaces exposed to radiant heat. Fouling is defined as the formation of deposits on convection surfaces such as superheaters and reheaters [101]. The viscosity of the coal ash slag determines the diffusivity of ions within the slag that affects its corrosivity [106].

12.11.1 Inorganic Analysis for Grassy Biomass and Agricultural Residues

Reza et al. performed a detailed inorganic analysis for four different biomass (i.e., corn stover, miscanthus, switch grass, and rice hulls), which have relatively high inorganic content. HTC treatment resulted in a reduction of slagging tendency for every biomass except corn stover (Table 12.2). An intermediate tendency of slagging for raw feedstocks, HTC 230, and HTC 260 are found for corn stover, while, HTC 200 has the highest slagging tendency. Fouling index data indicated that the fouling tendency improved in HTC 260 for all biochars compared to the starting biomass feedstocks. With respect to ratio slag viscosity (IV), only raw corn stover showed a medium slagging tendency, which was low for the other raw biomass and every HTC biochar. Cl was found to be high in raw and HTC 200 switch grass, but was low for every other HTC biochar. In terms of alkali index (IA) only raw corn stover, miscanthus, switch grass, and HTC 200 corn stover showed a probable tendency for slagging. But with increased HTC temperature, the alkali index was found to be low for every biochar.

12.11.2 Heavy Metal Analysis of HTC Biochar

Heavy metals like Hg, Pb, Cd, Cr, Cu, Zn, As, Ni, Ag, and Se exist in trace amounts in biomass. Nevertheless, in using HTC biochar and handling its ash, data about heavy metal content is essential due to environmental issues. Table 12.3 shows the heavy metal content in HTC biochar for corn stover, miscanthus, switch grass, and rice hulls. Hg and Se concentrations are below the detection limit of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Heavy metals are found in this range: 1–20 mg Ni, 5–17 mg Ag, 27–34 mg Pb, 6–45 mg Zn, 3–14 mg Cu, 1–44 mg As, 9–52 mg Cd, and 2–14 mg Cr per kg of raw biomass. Only Cd for all raw biomass and As for raw rice hull exceeds the soil protection act limit. These heavy metals have high melting points and as a result they are concentrated in the ash after combustion, sometimes by an order of magnitude. There could be compliance issues in disposal of raw biomass ash. Low

Table 12.2 Slagging, fouling, alkali, and ratio-slag indices, Cl content, definition, and their limits [103]

Slagging/fouling index	Expression	Limit
Slagging index	$I_s = (B/A)^* S^d$ $S^d = \%$ of S in dry fuel	$I_s < 0.6$ low slagging inclination $I_s = 0.6–2.0$ medium $I_s = 2.0–2.6$ high $I_s > 2.6$ extremely high
Fouling index	$I_F = (B/A)^*(Na_2O + K_2O)$	$I_F \leq 0.6$ low fouling inclination $0.6 < I_F < 40$ medium $I_F \geq 40$ high
Alkali index	$I_A = (Na_2O + K_2O)$ in kg/GJ	$0.17 < I_A < 0.34$ slagging/fouling probable $I_A \geq 0.34$ slagging/fouling is certain
Slag viscosity index	$I_V = (SiO_2{*}100)/(SiO_2 + MgO + CaO + Fe_2O_3)$	$I_V > 72$ low slagging inclination $65 \leq I_V \leq 72$ moderate $I_V < 65$ high
Chlorine content	Cl as received (%)	Cl < 0.2–0.3 low slagging inclination 0.2 < Cl < 0.3 medium 0.3 < Cl < 0.5 High Cl > 0.5 extremely high

Group A: Fe_2O_3, CaO, MgO, Na_2O, or K_2O. Group B: SiO_2, Al_2O_3, & TiO_2. Reprinted from Ref. [107], Copyright 2013, with permission from Elsevier

Table 12.3 Slagging and fouling indices for HTC biochar. Reprinted from Ref. [107], Copyright 2013, with permission from Elsevier

Biomass	Condition	I_S	I_F	I_V	Cl	I_A
Corn stover	Raw	medium	high	medium	low	probable
	HTC 200	high	medium	low	low	probable
	HTC 230	medium	medium	low	low	low
	HTC 260	medium	medium	low	low	low
Miscanthus	Raw	low	medium	low	low	probable
	HTC 200	Medium	medium	low	low	low
	HTC 230	low	medium	low	low	low
	HTC 260	low	low	low	low	low
Switch grass	Raw	medium	medium	low	high	probable
	HTC 200	medium	medium	low	high	low
	HTC 230	low	medium	low	low	low
	HTC 260	low	medium	low	low	low
Rice hull	Raw	low	medium	low	low	low
	HTC 200	low	low	low	low	low
	HTC 230	low	low	low	low	low
	HTC 260	low	low	low	low	low

temperature HTC treatment is effective for heavy metal reduction. All the heavy metals except Pb and As are found concentrations less than 15 mg per kg of HTC 200 for every biomass [107]. Pb and As are relatively inert to HTC reactions.

In summary, HTC can be effective in reducing slagging and fouling, as well as hazardous heavy metals concentrations for biomass. If biomass is to be used for co-firing, using HTC on the higher ash content grassy and agricultural residues would be beneficial, both economically and environmentally.

12.12 Energy Balance: Heat of Reaction

Design of an industrial-scale reactor requires knowledge of the heat of reaction. For continuous design, other considerations will impact the amount of heat added or removed, especially including heat integration, water recycle, and amount and temperature of makeup water. Here, we consider only the heat of reaction, heat released (or consumed) by the chemical reactions of HTC of lignocellulosic biomass.

There has been little literature published in this area. Yan et al. [7] attempted to calculate the heat of reaction from the heats of formation of all reactants and products. The reaction products were simplified in the analysis. All sugars were considered to consist of either glucose (at 200 °C) or 5-HMF at higher temperatures. All acids were considered to be acetic acid for this analysis, and all gases were considered to be CO_2. The heat of formation for the char product was calculated from its ultimate analysis and from its HHV. The heat of reaction was calculated at three reaction temperatures (200, 230, and 260 °C), and the results showed that the heat of reaction was slightly endothermic, and appeared to become less endothermic with increasing reaction temperature. A significant shortcoming of that analysis was the failure to account for production of water during reaction. As shown in this chapter and elsewhere [61] the amount of water produced can be quite significant. Had water production been included in the analysis of Yan et al. [7], the result would have shown an exothermic reaction, with increasing exothermicity as reaction temperature increases.

Funke and Ziegler [108] reported on a different approach to measure the heat of chemical reaction. They used differential scanning calorimetry (DSC) with glucose, cellulose, and wood, and found an exothermic reaction in all cases, with $\Delta H \approx -1$ MJ/kg at 240 °C for reaction times between 4 and 6 h. Hydrolysis of the carbohydrate fractions of biomass (hemicellulose and cellulose) produces oligosaccharides and simple sugars, among many other produces. With time, oligosaccharides further degrade to simple sugars and subsequently to furfural and 5-HMF. Thus, the long reaction time employed by Funke and Ziegler includes hydrolysis of biomass, as well as that of the products of the initial hydrolysis, especially including aqueous phase reactants.

Neglecting the production of compounds other than water and CO_2, one can compute an upper bound to the amount of heat released during reaction. All carbon lost from the biomass can be assumed to become carbon dioxide, while the oxygen lost is apportioned between water and CO_2. With increasing severity of reaction, more of these two low-energy reaction products are produced, and it follows therefore that the reaction must be more exothermic with increasing reaction temperature and time. Funke and Ziegler reported a minimum exothermic heat of reaction of −2.4 MJ/kg for relatively severe reaction conditions of 310–340 °C and times greater than 64 h.

Clearly, more investigation is required to determine the heat of reaction of biomass HTC. The two published works above reference only woody biomass, and contain very little information on the effects of operating conditions. Nonetheless, it is possible to conclude generally that the heat of reaction is likely to be slightly exothermic. The amount of heat produced by reaction is likely to be insufficient to provide for the heat required to operate a continuous process, since heating water to reaction temperature requires significant amounts of heat. This motivates the need for innovative design to best recover process heat with the goal of minimizing the cost of fuels (biomass, char, or other) needed to operate the process at the designated operating conditions.

12.13 Pelletization

12.13.1 Pelletization Benefits

Since biochar particles are hydrophobic, discrete, friable, and less than 1 mm mesh size, they pose potential respiratory and fire hazards. Pelletization can effectively reduce these hazards. Pelletization compacts the biomass particles and, as a result, the mass density increases. HTC biochar pellets have higher mass and energy density. For instance, Table 12.4 shows that pellets from raw loblolly pine have a mass density of 1102.8 kg/m^3, while raw loblolly wood has a density of 813 kg/m^3. Pellets of loblolly pine pretreated at 260 °C have a mass density of 1462.8 kg/m^3, which is 32.6 % higher than the pellets of loblolly pine pretreated at 200 °C and 80 % higher than that of pellets made from raw loblolly pine wood. Yan et al. [8] reported that the product of hydrothermally carbonized lignocellulosic biomass is more friable with increasing pretreatment temperature and it becomes more hydrophobic.

HHV is almost the same for raw biomass and pellets, as shown in Table 12.4. HTC biochar's HHV is similar whether pelletized or not [6]. That implies that the chemical compositions remain the same through the pelletization process. The materials are compressed, without chemical reaction.

In terms of energy density, since the mass density of pellets increases rapidly and the HHV remains same, the energy density increases rapidly. Table 12.4 shows the energy densities of the pellets of pretreated loblolly pine. Pellets of pretreated loblolly pine at 260 °C have an energy density of 38.79 GJ/m^3 which is 70 % higher than raw loblolly pellets and 142 % higher than raw loblolly wood [6]. Table 12.5 shows the abrasion index for pellets of raw loblolly pine as well as

Table 12.4 Mass and energy density of loblolly pine wood, pellets of raw loblolly pine, pellets pretreated at HTC-200, HTC-230, and HTC-260.

	Mass density (kg/m^3)	HHV (MJ/kg)	Energy density (GJ/m^3)
Wood	813	19.5	15.9
Raw pellet	1102	20.6	22.8
HTC-200 pellet	1125	21.2	24.3
HTC-230 pellet	1331	22.5	30.0
HTC-260 pellet	1468	26.4	38.8

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Table 12.5 Abrasion index and durability of pellets of loblolly pine and HTC biochar pretreated at different temperatures.

Pretreated temperature (°C)	Abrasion index (%)	Durability (%)
Raw	1.03	98.1
200	0.47	99.5
230	0.28	99.7
260	0.18	99.8

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loblolly pine HTC pretreated at 200, 230, and 260 °C for a reaction time of 5 min. Abrasion index is the ratio of mass percentage below 1.56 mm mesh to the initial sample mass after 3000 rotations in a tumbler [109]. The smaller the abrasion index, the better quality is the pellet. Durability is inversely related to the abrasion index. Raw loblolly pine pellets have an abrasion index of 1 %, whereas the pretreated loblolly pine pellets have decreased abrasion index with increasing HTC reaction temperature. (Table 12.5).

In the case of pellets of HTC biochar, the abrasion index decreases with the increase of pretreatment temperature, when all the other variables are the same (Table 12.5). The lower abrasion index and higher durability mean the pellets are mechanically more stable. As lignin is inert in the temperature range of 200–260 °C, the lignin percentage increases in the HTC biochar with pretreatment temperature using the same reaction time [81]. Yan et al. [8] reported that the lignin percentage of HTC biochar pretreated at 260 °C is 35 %, while it is 25 % in the raw biomass.

12.13.2 Lignin as a Binder in Pelletization

12.13.2.1 Glass Transition Behavior of Lignin

Lignin is the only component of biomass that shows glass transition behavior [6]. Glass transition is a property of the amorphous portion of a semi-crystalline solid [110]. The crystalline portion remains crystalline during the glass transition. At a low temperature the amorphous regions of a polymer are in the glassy state, where

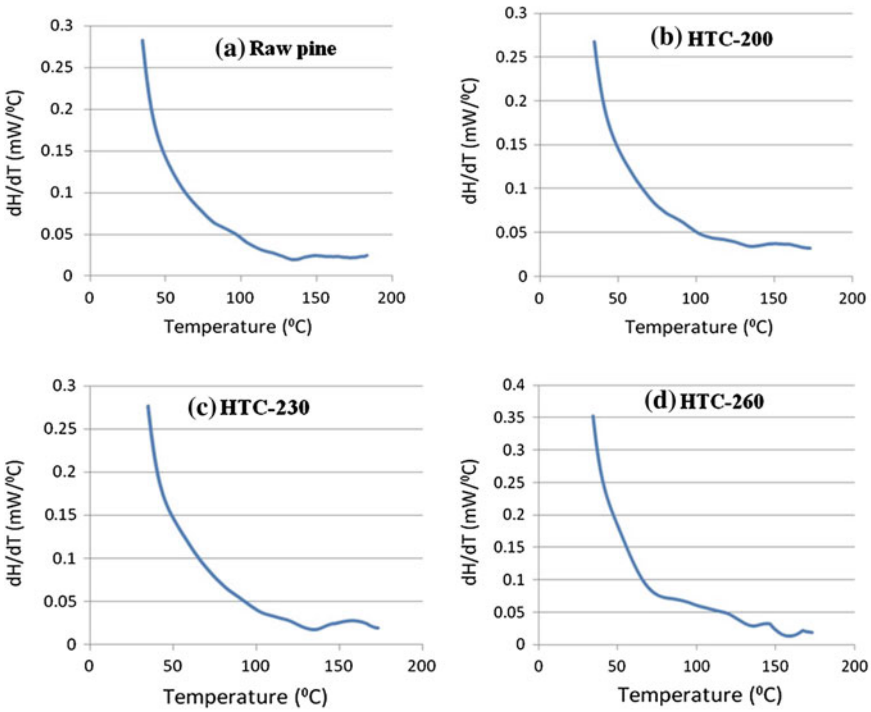

Fig. 12.8 DSC curves (slope of heat flow versus temperature) for determination of glass transition temperature of extracted lignin from HTC biochar and raw loblolly pine. Reproduced from Ref. [6] by permission of John Wiley and Sons Ltd

the molecules are frozen in place. They may be able to vibrate slightly, but do not have any segmental motion in which portions of the molecule rotate. When the amorphous regions are in the glassy state, the polymer generally will be hard, rigid, and brittle [110]. Lignin extracted by fiber analysis showed a glass transition change when undergoing digital scanning calorimetry (DSC), as shown in Fig. 12.8. The lignin extracted from raw loblolly pine and HTC biochar showed a range of glass transition temperature of 135–165 °C in the heat flow curve versus temperature. At a temperature of 135 °C, the slope starts increasing with temperature until 165 °C, and then it follows the same trend again. The change of heat flow pattern with temperature over the range of 135–165 °C indicates the glass transition behavior of lignin [111].

12.13.2.2 SEM Images of HTC Biomass Pellets

At temperatures higher than its glass transition temperature, lignin acts as a binder causing liquid bridges to develop between adjacent particles. In most cases, an immobile thin adsorption layer is produced by the binder which attaches the

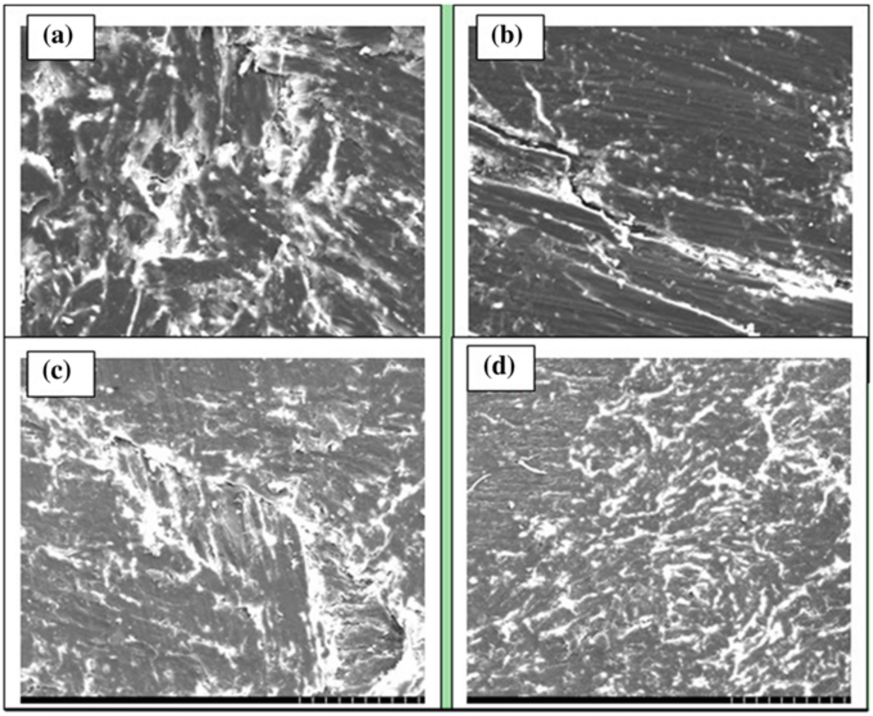

Fig. 12.9 SEM images (200 times magnification) of **a** raw loblolly pine pellet. **b** HTC-200 biochar pellet. **c** HTC-230 biochar pellet. **d** HTC-260 biochar pellet. Reprinted from [56] with permission

particles by effectively reducing surface roughness or decreasing inter-particle distance Attractive forces then come into action resulting in binding and the formation of stable bonds [112]. Lower particle sizes and smaller distances among the particles encourage liquid bridge building [110]. Applying compression reduces interparticle distances and particle size, if the particles are friable. So, pressure is required as well as temperature to activate binding mechanisms among the particles. SEM images can be used to illustrate this binding process.

The raw pine pellet shown in Fig. 12.9a is smooth and seems to have a good solid bridge on the surface. No significant cracks are observed in Fig. 12.9a. But cracks are observed in the HTC biochar pellets. The crack in the HTC-200 biochar pellet is larger than that of the other HTC biochars or even raw pine pellets. HTC biochar has only lignin as a binder as all the water extractives and other natural binders are extracted or destroyed during HTC [109]. The lignin percentage of HTC-200 biochar is probably not enough to fill up the cracks. The crack in the HTC-230 biochar pellet in Fig. 12.9c is smaller than that of HTC-200 biochar pellet, while no significant crack is observed in the HTC-260 biochar pellet in Fig. 12.9d. The percentage of lignin in the HTC-260 biochar pellet is enough to form solid bridges among the particles and make the pellet durable.

12.14 Conclusions

In this chapter, we have discussed the history of HTC of biomass, and reviewed the recent literature. Much has been published recently on HTC of diverse biomass feedstocks, and effects of temperature, time, and pH have been reported, but there is still much left to learn. A picture of the underlying chemistry of HTC is beginning to emerge, but further knowledge is required, especially to learn how to use process parameters to affect desired product characteristics.

HTC pretreatment of lignocellulosic biomass presents unique advantages and unique challenges. In many regard, the process can be viewed as one that mimics earth's natural process of converting biomass to coal, but accelerates the time from millennia to minutes. The solid product has a high energy density, is friable, is easily pelletized, and is very hydrophobic. On the other hand, this is a high pressure process with concomitant capital costs.

A pressing need is development and deployment of pilot scale facilities. Continuous operation of an HTC process presents technical challenges, including: feeding solid and liquid into a high pressure reactor, heat integration, separation and recycling of water without flashing. The experience gained from operating long-term operations will be invaluable in determining the commercial viability of HTC. In particular, capital costs are currently unavailable, and erosion rates and maintenance requirements are entirely unknown.

Further work is required to characterize the aqueous byproducts, which include many useful components, such as organic acids, sugars, and furfurals. A low-cost process to convert these compounds to chemicals or fuels would significantly enhance the commercial prospects of HTC.

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